Bull. Environ. Contam. Toxicol. (1988) 40:655-659

Bulletin of Environmental Contamination and Toxicology

Rapid Technique for Thiobencarb Residue Determination in Rice Samples

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In recent years, substantial amounts of chemicals and pesticides have been used by the agriculture industry (Storck 1984). However, little attention has been given to the detection and quantitation of Thiobencarb residues on processed food products. Data on the health effects of this pesticide residues are scanty.

Thiobencarb S-(4-Chlorobenzyl-N,N-diethylthiocarbamate) (Ishikawa et. al. 1973; Kimura et. al 1971; Nakamura et. al 1974; Richard Jr. et. al. 1981) a newly introduced, excellent herbicide for barnyardgrass, sprangletop, dayflower and aquatic weeds, is used extensively by the California rice growing industry. Hence, it has been selected as one of the pesticides to be monitored in the California food protection program.

The separation of thiobencarb from rice is usually performed by liquid-liquid extraction, a lengthy procedure (Nakamura et. al. 1977; Suzuki et. al. 1977). Due to the number of samples to be processed during this program, the existing method would require a tremendous number of man-hours. The purpose of this study is to develop an expeditious alternative method by reducing the extraction period.

MATERIALS AND METHODS

Thiobencarb standard was obtained from the US Environmental Protection Agency, Pesticide and Industrial Chemical Repository(MD-8, Research Triangle Park, NC 27711). All other reagents were obtained from local suppliers.

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Weigh standard in a 10 ml volumetric flask. Add methanol or acetone to volume. Make appropriate dilutions for recovery and linearity studies.

Add 0.07 ml of 1.44 mg/ml thiobencarb standard to 25 gm of rice in a 100 ml beaker. Mix well. Wait till the sample becomes dry. Decant the rice sample into a 500 ml container of an Omni-mixer. Add 100 ml of methanol or acetone to the container, and blend for one minute. Decant the extract into a screw cap tube. Inject 1 to 5 µl of extract into a Varian 3700 Gas Chromatograph equipped with TSD and ECD and Tracor MT 220 Gas Chromatograph equipped with FPD.

Add 0.07 ml of methanol or acetone to 25 gm of rice and proceed as described in the preparation of fortified sample.

A 200 cm x 6.36 mm x 2 mm glass column containing 1.5% OV- 17/1.95% OV- 210 on 80/100 Gas Chrom Q was used with a Varian 3700 Gas Chromatograph equipped with ECD and TSD. The chromatographic conditions for ECD and TSD were as follows. The injector temperature was set at 220° C and the detector and column temperature were set at 250°C and 210° C respectively. Nitrogen, the carrier gas, was set to a flow rate of 30 ml/min.; with TSD, the flow rate of hydrogen was 4.5 ml/min. and that of air was 175 ml/min.

A 200 cm x 4cm. i.d. glass column containing 1.5% OV-17/1.95% OV-210 on 80/100 Gas Chrom Q was used with Tracor MT 220 Gas Chromatograph equipped with an FPD (sulfur mode). Nitrogen was used as carrier gas and the flow rate was set at 80 ml/min. The flow rate of air was 100 ml/min, and that of hydrogen was 50 ml/min. The injector temperature was set at 230° C while the detector and column temperature were set at 210°C.

RESULTS AND DISCUSSION

Figures 1A and 1B show the response of FPD and TSD to thiobencarb in methanol extract recovered from fortified rice samples. The interference generated from other compounds in the methanol extract was so large that thiobencarb could not be detected by ECD. However, the substitution of acetone as solvent for extraction alleviates the problem by substantially reducing the EC interference from other compounds, and thiobencarb can be detected by all three detectors as shown in figures 2A, b and C. The recovery of thiobencarb is found to be 95% with methanol and 104% with acetone extraction. Linear range can be established with all three detectors. The extraction method described in this study not only shortens the

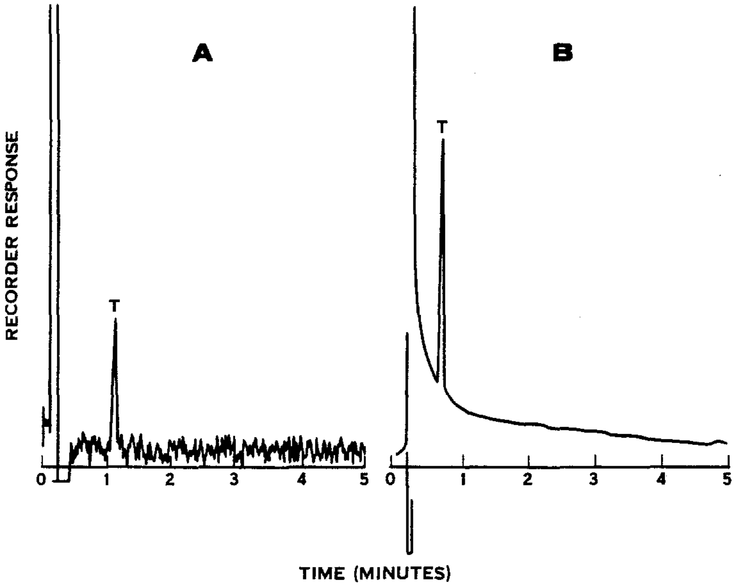

Figure 1. (A) Flame Photometric Detector response to methanol extract from rice fortified with thiobencarb and (B) Thermionic Specific Detector response to methanol extract from rice fortified with thiobencarb. For experimental details, see "Materials and Methods" section. T for Thiobencarb.

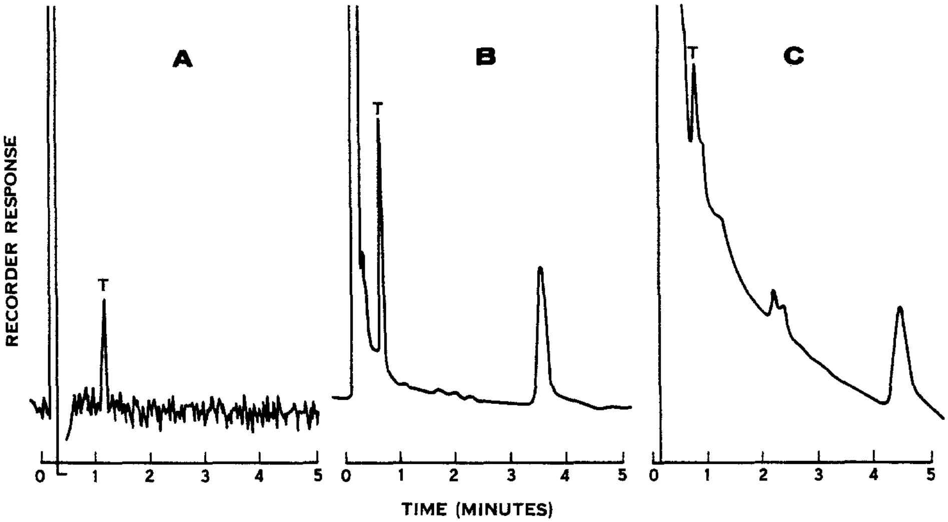

Figure 2. Gas Chromatographs of acetone extract from rice fortified with thiobencarb (A) with Flame Photometric Detector (B) with Thermionic Specific Detector and (C) with Electron Capture Detector. For experimental details, see "Materials and Methods" section. T for Thiobencarb.

time of preparation of samples, but also reduces the number of solvents and the amount of each solvent used. Since no clean up is required with this procedure, the flash vaporization technique is the preferred mode for introduction of the sample into the gas chromatograph. This mode avoids any premature detector contamination.

ECD, probably the most common gas chromatograph detector, is relatively simple to operate. In this study with thiobencarb, ECD gives an approximately ten-folded advantage in sensitivity when compared with FPD. Thus, ECD is the detector of choice for thiobencarb analysis. The blending of rice with methanol generates interferences with ECD, while extraction with acetone eliminates most of the ECD specific interferences stemming from methanol extraction. Therefore, if an ECD is used, acetone should be substituted for methanol.

Even though some of the interferences that were in the ECD chromatogram (Figure 2C) also appeared in the TSD chromatograms, TSD (as shown in figure 2B) provides a very distinct thiobencarb peak. This coupled with the fact that TSD has sensitivity equivalent to ECD makes it an attractive alternative detector.

FPD has been widely used for the detection of thiobencarb (Duah-Yentumi et. al. 1982; Suzuki et. al. 1977). However, compared to ECD or TSD, the sensitivity of FPD is relatively low. Unlike ECD and TSD, the interferences do not show up in the FPD chromatogram. The actual chromatographic run of figures 1A and 2A were carried out over an extended period of time and no extraneous peaks were found.

Au et. al.(1984) pioneered the use of C18 Reverse-phase solid sorbents substitute for liquid-liquid extraction of thiobencarb from water samples. In this study, a modification of this method was carried out to accommodate the use of rice samples Use of C18 adsorbents eliminates some, but not all, of the interferences, but it was found that recovery was at best 30%. Since the extraction procedure presented in this communication gives essentially quantitative recovery, the C18 adsorbent approach offers no improvement in the analysis of thiobencarb in rice samples.

At present, the identities of the interferences are not known. Further study with gas chromatograph/mass spectroscopy will be undertaken to determine their structures. If the structures of the interferences can be established it may be possible to devise a modification of the method to remove these high electron affinity and nitrogen containing compounds.

In conclusion, the present studies establish that thiobencarb residue on rice can be detected by gas chromatography both with ECD and with TSD as as well as by the conventional FPD. Thiobencarb can be readily extracted from rice samples by either methanol or acetone and either extract can be injected directly onto a gas chromatographic column without further treatment.

Acknowledgments. The authors gratefully acknowledge Ms. Hazel Anderholm for preparing the figures for publication, Professor M. F. Dunn and Dr. T. Belsky for critical reading of this manuscript.

REFERENCES

Au AM, Tamplin BR, Khalifa S (1984) Analysis of thiobencarb: An HPLC approach. Liquid Chrom & HPLC 2:122-123

Duah-Yentumi S, Kuwatsuka S (1982) Microbial degradation of benthiocarb MCPA and 2,4-D herbicides in perfused soils amended with organic matter and chemical fertilizers. Soil Plant Nutr 28:19-26

Ishikawa K, Okuda I, Kuwatsuka S (1973) Metabolism of benthiocarb (4-Chlorobenzyl N,N-Diethylthiocarbamate) in mice. Agr Biol Chem 37:165-173

Kimura I, Ichizen N, Matsunaka S (1971) Mode of action of herbicide, benthiocarb. Weed Res 12:54

Nakamura Y, Ishikawa K, Kuwatsuka S (1974) Uptake and translocation of benthiocarb herbicide by plants. Agr Biol Chem 38:1129-1135

Nakamura Y, Ishikawa K, Kuwatsuka S (1977) Degradation of benthiocarb in soils as affected by soilconditions. J Pest Sci 2:7-16

Richard Jr EP, Miller TC, Bowman DH (1981) Control of barnyardgrass in rice with thiobencarb. Mississippi Agr & Forestry Exp Station Res Report 6:1-3

Storck WJ (1984) Pesticides head for recovery. Chem & Engineering News April 9:35-59

Suzuki M, Yamato Y, Akiyama T (1977) Occurence and determination of a herbicide benthiocarb in rivers and agricultural drainages. Water Res 11:275-279

Received October 24, 1987;accepted December 31, 1987.